Nonvolatile Acids of Cigar Smoke

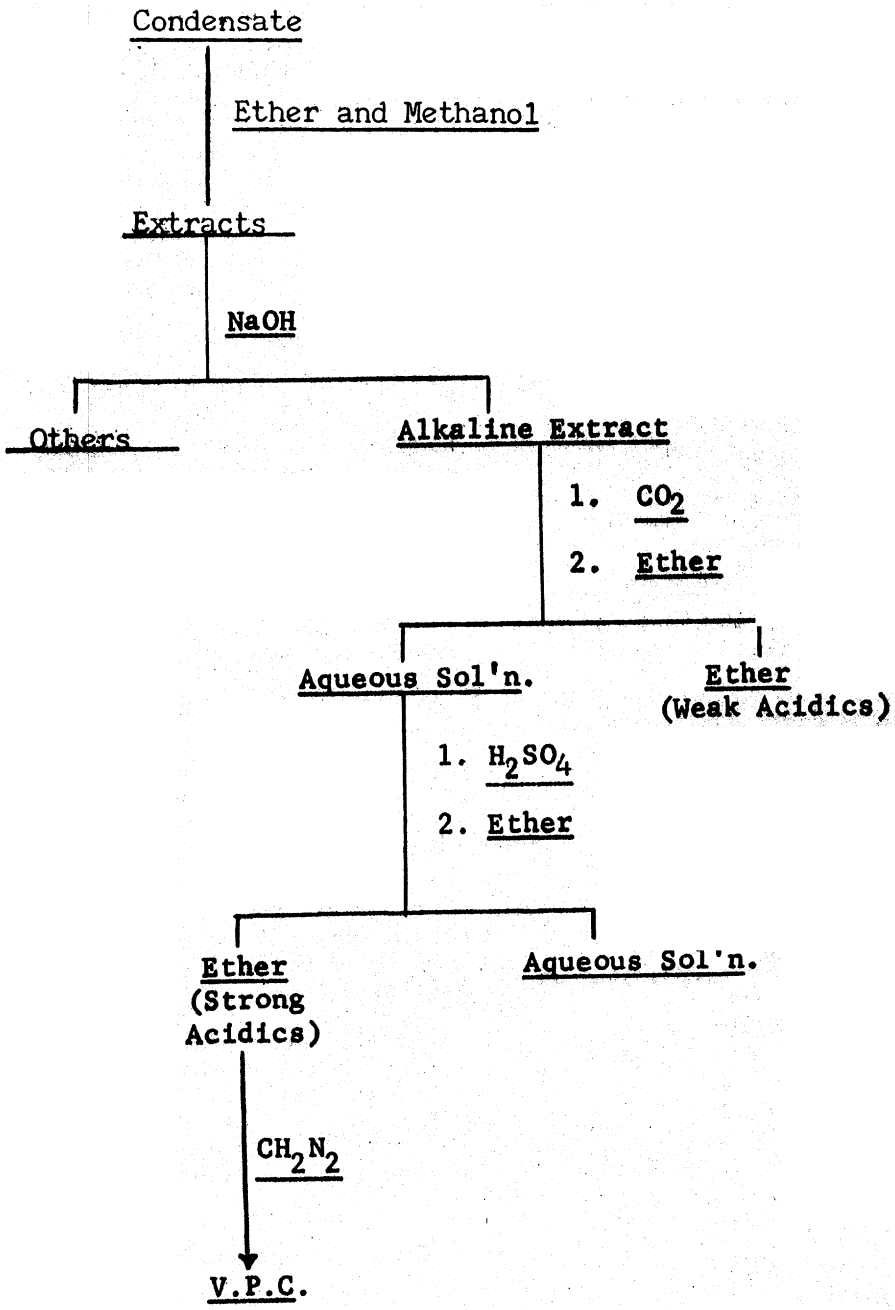
Introduction

Reports by Quin and co-workers (1958, 1961) on the nonvolatile acids of cigarette smoke have recently appeared. Using gas chromatographic techniques, these workers identified at least eleven acids and made semi-quantitative estimates of their amounts in cigarette smoke. The present report describes a similar study on the nonvolatile acids of cigar smoke.

Experimental

Collection of Smoke. The smoking machine and other experimental conditions have been previously described (Schepartz, 1959, 1960; Schmeltz and Schlotzhauer, 1961). The cigars were the same brand of panatella with all-Havana filler and drawn tuck which was previously used in a study of volatile acids (Schmeltz and Schlotzhauer, 1961).

Fractionation of Cigar Smoke Condensate. The acids were extracted from smoke condensate as outlined in **Figure 1.** As a representative example the condensate from 40 cigars was extracted successively with ether (100 ml. total) and methanol (100 ml. total) which dissolved the entire residue. The ether solution was extracted thrice (100 ml. each) with 0.5% sodium hydroxide. The methanolic solution was evaporated *in vacuo*, and the residue partitioned between 0.5% sodium hydroxide and ether (50 ml. each). The two alkaline solutions were then pooled, and carbon dioxide was passed through the solution for one hour during which a precipitate was formed. The sus-



[1] *Presented at the Fifteenth Tobacco Chemists' Research Conference, Philadelphia, Pennsylvania, October, 1961.*

[2] *Senior and Junior Research Fellows, respectively, Cigar Manufacturers Association of America.*

[3] *Eastern Utilization Research and Development Division, Agricultural Research Service, United States Department of Agriculture.*

pension was then extracted continuously for 48 hours with 300 ml. ether to remove the precipitated weakly acidic material which will be the subject of a future publication. The aqueous solution was then strongly acidified with concentrated sulfuric acid and reextracted continuously with ether (300 ml.) for an additional 48 hours. The resulting ether solution containing the strongly acidic substances was then evaporated to dryness *in vacuo*. The brown, semisolid residue was dissolved in 10 ml. ether-methanol (1:1), and the solution was mixed with an ethereal solution (25 ml.) of diazomethane which was prepared from 3 g. nitrosomethylurea by the method of Arndt (1943). The solution was stored at 0° C for one hour and then overnight in the refrigerator after which it was evaporated to dryness *in vacuo* and the residue of methyl esters taken up in ether. The ether solution was dried over anhydrous sodium sulfate, and concentrated to a volume of 1 ml. Usually the condensate from 16-20 cigars prepared in this manner contained sufficient material for gas chromatographic study as described below.

Gas Chromatography. An Aerograph Model A-350 Temperature Programmer[4] having a thermal conductivity cell as the detector was used for the gas chromatographic studies. Twenty percent butanediol succinate polyester (Craig) on firebrick and 20% Carbowax-20M on Chromosorb (each 5 ft. in length and ¼ in. O.D.) gave satisfactory separations of the methyl esters when 20 μl. aliquots of the above solutions were injected. Helium served as carrier gas with a flow rate of 45 ml/min. Optimum column temperatures were 155° C and 200° C. Most of the esters produced sharp peaks at 155° C. Some of the higher boiling components, however, were detected at the higher temperature. In general, the chromatograms were qualitatively similar to those described by Quin (1958). The procedures of Quin *et al.* (1958, 1961) were used for identifications and estimations of quantities.

Results and Discussion

A total of twenty-one peaks were obtained in initial screening of the fractions using temperature-programming from 88° C to 210° C. The major peaks and amounts of each peak were determined using the previously described isothermal conditions. The data are presented in **Table 1.** The remainder of the peaks were minor acids and have not been identified.

Table 1. Nonvolatile acids of cigar smoke

Acid	Mg/100 Cigars smoked*	Mg/100 g Tobacco smoked**
Succinic	7.8	1.43
Furoic	5.8	1.07
Lactic	5.2	0.96
Oxalic	4.5	0.83
Glycolic	3.6	0.66
Levulinic	2.9	0.53
Benzoic	2.6	0.48
Malic	2.0	0.37
Phthalic	1.9	0.35
Glutaric	1.1	0.20
Adipic	< 0.1	< 0.02
Palmitic	< 0.1	< 0.02

**100 cigars contained 800 g tobacco.*
***Sixty-eight percent of cigar consumed during smoking.*

All the identified acids have been found previously in cigarette smoke (Quin *et al.*, 1958, 1961). However, the levels of cigar smoke acids per gram of tobacco smoked are lower than those reported for cigarette smoke (Quin *et al.*, 1961). A similar relationship for the volatile acids of cigar and cigarette smoke has been noted (Schmeltz and Schlotzhauer, 1961).

Benzoic acid has been isolated from cigarette smoke condensate as a volatile (steam-distillable) acid (Buyske *et al.*, 1957). The level of benzoic acid in cigar smoke may, therefore, be higher than the estimate given in **Table 1.**

Summary

By means of continuous extraction procedures, methylation with diazomethane, and gas chromatography of the methyl esters, the following nonvolatile acids were isolated from cigar smoke condensate: lactic, glycolic, oxalic, furoic, succinic, levulinic, benzoic, glutaric, adipic, malic, phthalic and palmitic. Estimates of amounts of these acids were made and were found to be lower than those reported for cigarette smoke on the basis of weight of tobacco smoked.

Acknowledgment

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[4] Mention of a specific commercial product does not constitute an endorsement by the United States Department of Agriculture over similar items not named.